X-ray diffraction, photoluminescence and composition standards of compound semiconductors[*]

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Work is underway to develop composition standards and standardized assessment procedures for compound semiconductors. An AlGaAs composition standard with less than 2% uncertainty is being developed. The improved accuracy of this standard is being achieved by combining an array of analysis techniques, including reflection high energy electron diffraction, photoluminescence (PL), electron microprobe analysis and inductively coupled plasma–optical emission spectroscopy. A major part of the work has been quantification of the accuracy limits of each technique. The influence of peak fitting method, measurement temperature, and doping concentration on PL measurements of AlGaAs layers has been measured. Similar work is underway for PL analysis of InGaAsP and for X-ray diffraction (XRD) analysis of a wide variety of materials in order to develop standardized assessment procedures. An inter-laboratory comparison was made of XRD and PL measurements of InGaAsP layers. The study demonstrated that material nonuniformity dominated the variation in the XRD measurements; but the uniformity was sufficient to allow PL measurement variations to be assessed.

1. Introduction Accurate characterization of III–V semiconductor alloy film composition is critical for applications in lasers, detectors, and light-emitting diodes. However, lack of standardized assessment procedures and of an absolute composition scale have been identified as major impediments to semiconductor device production in the optoelectronics industry. Most laboratories use their own internal calibration standards and can measure the relative composition of their materials with high precision, but low accuracy. Thus, problems arise when they share materials or material parameters with other laboratories, because of large variations in composition assessment between laboratories. Contributing to this problem is a lack of composition standards for inter-laboratory calibration of the more common analytical techniques.

NIST has several different efforts that address different aspects of these issues. One is developing AlGaAs composition standards with uncertainties less than 2% in mole fraction. Another involves studies to develop standardized X-ray diffraction (XRD) and photoluminescence (PL) assessment procedures for InGaAsP layers on InP substrates. A third is putting together a consortium to study high-resolution X-ray analysis methods. The goal of all these efforts is to enable industry, university, and government laboratories to exchange materials and materials data with confidence that they are using the same assessment procedures and composition scale.

2. AlGaAs composition standards   Most laboratories can measure compound semiconductor alloy composition with high precision, but low accuracy, based on their own internal composition standards, to assess reproducibility of material growth. However, in order to achieve a uniform, standardized composition scale that allows comparisons between laboratories, NIST is developing high-accuracy AlGaAs composition standard reference materials (SRMs) with mole fractions specified to better than ±0.003.

This is a ten fold improvement over the accuracy of techniques currently in use by industry (typically PL and XRD). In 1994 a group of molecular beam epitaxy (MBE) crystal growers conducted an interlaboratory comparison of composition assessment with specimens from a single $Al_xGa_{1-x}As$/GaAs wafer with a nominal Al mole fraction of $x = 0.25$ [1]. Evaluations by eleven different laboratories yielded a range of results from $x = 0.24$ to 0.34, with an implied uncertainty of at least 0.05 mole fraction, more than ten times greater than the goal of the work described here.

The increased accuracy of the current work is being achieved through a combination of conventional composition determination methods, such as PL and XRD, with less common methods, such as *in-situ* monitoring, electron microprobe analysis (EMPA) and quantitative chemical analysis. The samples for the study are being grown by MBE, which is inherently stable and offers good reproducibility. Also, because it is a vacuum technique, MBE allows *in-situ* methods such as reflection high energy electron diffraction (RHEED). *In-situ* measurements provide new information not available from *ex-situ* techniques, since they can be used to measure the film as a function of time during growth.

RHEED intensity oscillations, measured prior to each growth run, are used to make the initial composition determination and to assess growth stability [2]. For each growth run the Al, Ga, and combined Al and Ga growth rates are measured from RHEED data and used to determine the film composition. Analysis of RHEED data taken under different conditions demonstrated that the largest uncertainty in the growth rate measurement comes from variations of the flux across the specimen. Also, interference between RHEED signals from different parts of large specimens can introduce a systematic error of about 2% in the measured growth rate. Flux transients were found to contribute errors up to 3%, depending on growth conditions. Examples of large flux transients measured by RHEED are given in Fig. 1, which is a plot of the "instantaneous" Al growth rate measured in three successive runs. The transient is due to the slight cooling of the cell following the shutter opening. It cannot be avoided, but it affects only a thin layer close to the substrate interface. The growth rate also depends on the effusion cell temperature and fill level. By minimizing and making corrections for these sources of error, the overall uncertainty in the RHEED measurements can be reduced to about 1% relative.

Because it gives a direct measure of the elemental compositions, wavelength dispersive EMPA was the primary tool used to establish Al mole fraction. The elemental lines used for the EMPA were chosen to avoid interferences from overlapping lines and to minimize uncertainties in the corrections. For each specimen the Al K-line, the Ga L-line, and the As K- and L-lines were measured at two accelerating voltages. The primary composition standards used were GaAs and Al_2O_3. After evaluation of several different correction procedures, it was determined that the NIST CITZAF procedure [3] yielded the most reliable, reproducible results [4] (CITZAF stands for: California Institute of Technology (CIT), atomic number (Z), absorption (A), and (characteristic) fluorescence (F) – the three main physical corrections applied to X-ray emission data in order to yield elemental concentrations). The uncertainty values for EMPA were based on the standard deviation of different combinations of the maximum and minimum possible Al, Ga, and As weight percents derived from the raw data; they indicate an uncertainty of ~1%. The use of two accelerating voltages allowed cross-correlations as a self-consistency check [4]. Discrepancies between RHEED and EMPA results were observed for samples with high Al contents (Al mole fraction $x > 0.5$), probably resulting from the inability of the current model to handle the GaAs cap required on these specimens. A cap is needed on samples with greater than 0.5 mole fraction Al to prevent oxidation of the AlGaAs layer. Future attempts will be made to correct the EMPA data for the effects of the GaAs cap layers.

The analytical chemistry technique being used is inductively coupled plasma–optical emission spectroscopy (ICP–OES), in which the films are dissolved in acid and the resulting solution is injected into an atmospheric pressure Ar plasma for analysis. Atomic emission intensities are measured and compared with intensities measured for calibration materials, to determine the film composition [5]. The technique
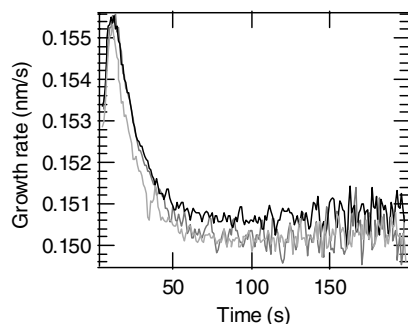
Fig. 1 Large flux transients in the growth rate measured by RHEED. The transients are due to cell cooling after the shutter opens.
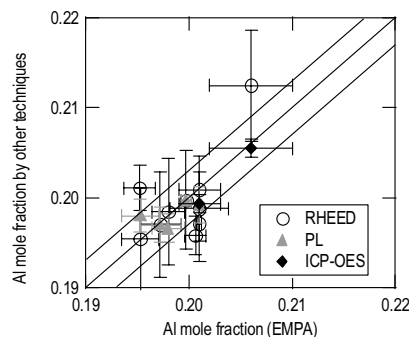

Fig. 2 Comparison of mole fraction determinations for multiple samples with various techniques: EMPA, RHEED, PL, and ICP–OES.

has an inherent uncertainty of 0.1 to 0.5% in mole fraction (0.0002 to 0.0010 for $x = 0.2$) [6]. For the AlGaAs samples, calibration was performed with the NIST Spectrometric Solution SRMs (3100 Series), making the ICP–OES results directly traceable to the mole. The first series of experiments has been conducted on films that were removed from the substrate using an epitaxial lift-off method [7]. The films are grown on pure AlAs buffer layers, coated with a protective wax, and then removed from the substrate by dissolving the AlAs in HF acid. The films are then bonded to Si and analyzed by PL, EMPA and ICP–OES. Contamination of the solution by the GaAs substrate would induce error; new samples for analysis are currently being grown on Ge substrates to eliminate this possibility. Because ICP–OES is a destructive technique it cannot be used on the actual SRM specimens. But, analyses at several different Al mole fractions will allow placement of the composition on an absolute, traceable scale, and comparisons with the other measurement techniques will give quantitative uncertainty analyses.

The results of measurements by the different techniques, on samples with Al mole fractions close to 0.2, are plotted in Fig. 2 against the EMPA analysis. The larger uncertainty in the EMPA than in the ICP–OES is evident from the larger horizontal than vertical error bars on the ICP–OES data points. The scatter in the RHEED data is likely the result of drifts in the evaporator cell fluxes between the time the RHEED measurements were made and when the layers were actually grown. Good agreement was found for the PL measurements, and details of these will be discussed below. There are no apparent trends in the composition differences, indicating that there are no systematic biases in any of the analysis techniques.

This work is being used to develop an $Al_xGa_{1-x}As$ composition SRM with $x = 0.20 \pm 0.003$. The standard is expected to be ready for distribution by the beginning of 2003. Information will be available from the NIST Standard Reference Materials Program [8]. Future work will be directed at standards with other Al mole fractions and in the InGaAsP system.

3. Accuracy of PL and XRD analysis   Another area of research is quantification of the uncertainty limits of the *indirect* composition measurement techniques currently in use by industry: PL and XRD. These techniques are indirect because they measure, respectively, bandgap and lattice parameter rather than actual composition. The two major factors limiting these techniques are poor understanding of the experimental parameters controlling accuracy, and inadequate modeling parameters for extracting composition from the measurements. The second issue is being addressed through production of certified composition standards, which will enable sharing of materials data. For the first issue, experiments are being conducted to identify the influence of specific parameters on the measurements.

As part of the work related to the AlGaAs composition standards, the effects of various parameters on the accuracy of PL measurements of AlGaAs film composition were studied. In this study, the peak of the photon emission spectrum, in units of energy, was correlated with the Al mole fraction, which was
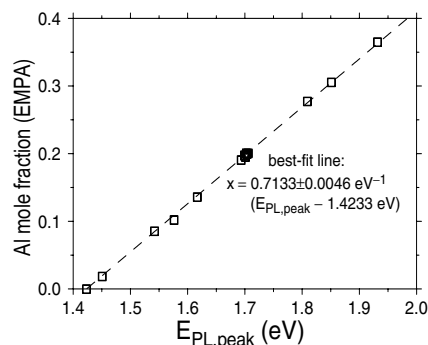
Fig. 3 Dependence of PL peak energy on Al composition, determined by EMPA, for thirteen specimens with carrier concentrations less than 10^{17} cm^{-3}. The best fit line is shown.

determined independently by a direct composition measurement methods (such as EMPA). The correlation, shown in Fig. 3, was found to be linear, within the measurement accuracies. Limitations in the accuracy of the PL-based composition measurements come from uncertainties in the correlated direct measurement and from PL measurement errors (photon energy determination and external effects). The uncertainty in the photon energy measurement was minimized through careful calibration of the photon energy scale and spectrometer response and by fitting the corrected data using an asymmetric bell-curve function. Important external parameters identified include ambient temperature, excitation intensity, and n-type or p-type doping level (carrier concentration). A linear relationship between temperature and apparent Al mole fraction was found, between 20 and 60 °C. Temperature effects were minimized by first measuring the temperature coefficient of the peak energy as a function of Al mole fraction and doping level, then correcting for any temperature drift detected during the PL measurements. Measurements of samples with different doping levels showed that doping concentrations above 10^{17} cm^{-3} measurably shifted the PL peak. Heavy n-type doping shifted the peak to higher energy, while heavy p-type doping shifted the peak to lower energy. Doping level effects were minimized by including only samples with carrier concentrations $\leq 10^{17}$ cm^{-3} in the PL-composition calibration set. Other factors that have been investigated include reproducibility and long-term drift. Details of the PL studies will be available in a forthcoming publication [9].

Similar studies have been initiated for both X-ray diffractometry and reflectometry. These measurements also may be influenced by sample temperature, impurities and/or doping level, peak fitting methods, and system calibration. In addition, the effects of hardware and software configurations, noise levels, specimen alignment, and analytical procedures on accuracy and precision will be addressed, with the goal of developing recommended measurement methods. Part of this work is being performed in the NIST Consortium for High-resolution X-ray Calibration Strategies (CHiXCS) [10].

4. InGaAsP interlaboratory comparison   In an effort to develop standardized assessment procedures for InGaAsP, an interlaboratory comparison of PL and XRD rocking curve measurements of a set of six specimens was performed. The samples are 1 μm thick InGaAsP films grown on slightly misoriented, 52 mm (2-inch), (001), InP wafers by metal organic chemical vapor deposition (MOCVD). The InGaAsP layers have no cap layer, and there are two samples for each nominal emission wavelength of 1.1, 1.3 and 1.5 μm. The samples were measured with eight different XRD instruments and eight different PL instruments.

Preliminary maps of the X-ray rocking curve peak separation and the peak photoluminescence wavelength over the central 2×2 cm^2 region of each wafer revealed fairly large variations. Figure 4 is a contour plot of such an X-ray map of a wafer. The difference between the contour lines is 20 arcsec and the maximum difference over the area is 400 arcsec. To minimize the effect of these variations on the study, a 1 cm^2 piece was cleaved from the most uniform region of each wafer. Participants were asked to make their measurements as close to the center of the 1 cm^2 specimens as possible.
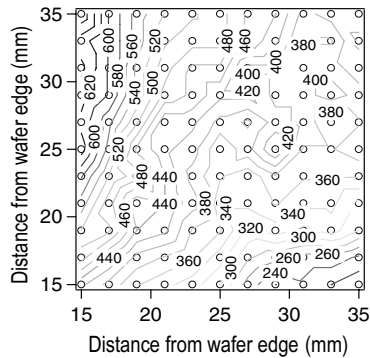
Fig. 4 Contour plot of X-ray rocking curve peak separation over central 2×2 cm^2 region of a wafer. The separation between the contours is 20 arcsec and the variation over the map is 400 arcsec.

The maximum difference in the XRD peak separation measured in a map of each 1 cm^2 specimen is given in the second column of Table 1. Also given in the table are the standard deviations of the measurements, in the center of each sample, from eight instruments (column 3) and the maximum difference between those measurements (column 4). For the X-ray analysis, the variation across each 1 cm^2 specimen is larger than the standard deviation in the measurements. The lateral specimen variation is also larger than the maximum difference between measurements in all but one case. Thus it is likely that differences in the position of the X-ray beam on the sample are responsible for the variations between measurements. Most of the participants in the study did not have experience making isolated measurements in a single spot on a sample. Material uniformity appears to have dominated the variation in the XRD measurements, causing the results to be more sensitive to beam positioning and peak identification than to other instrument and/or measurement differences.

Unlike the XRD analysis, the maximum variation in the PL peak wavelength mapped over each 1 cm^2 specimen (fifth column in Table 1) is smaller than the standard deviation of measurements by eight instruments at the center of the specimens (sixth column in Table 1). Thus the variations in the PL data represent instrument or technique related differences between the measurements. The deviation of the peak wavelength measured for each sample from the average is shown in Fig. 5. From the plot it can be seen that several instruments exhibit offsets (e.g., 6 and 7). These offsets could indicate calibration differences, although all but two of the instruments were reported to have been calibrated within three weeks of the measurements. Participants were also asked to report measurement conditions, such as temperature, spot size, beam power, and excitation wavelength. No correlation was found between the measurement conditions and the instrument offsets.

Table 1 Measurement statistics

specimen	XRD peak separation (arcsec)			PL peak wavelength (nm)		
	map max var	center std dev	center max var	map max var	center std dev	center max var
1	150	5.9	19	3	6.6	23.0
2	9	2.2	7	2	5.9	17.8
3	10	3.9	12	2	3.8	12.4
4	80	5.1	12	2	4.4	12.2
5	50	1.3	4	4	3.6	12.1
6	51	11.1	36.5	6	5.8	16.7

Columns 2 and 5 give the maximum variation in measurements mapping each 1 cm^2 specimen. Columns 3 and 6 give the standard deviation of measurements made at the center of each sample.
Columns 4 and 7 give the maximum variation in measurements made at the center of each sample.
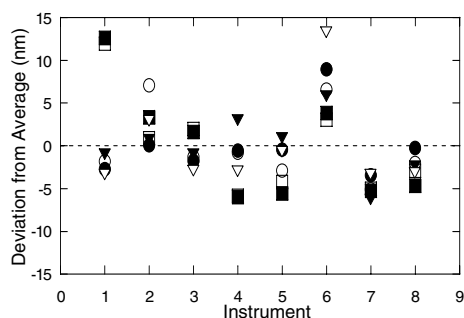
Fig. 5 Deviation of PL peak wavelength measured by eight different instruments from the average peak wavelength for each of six specimens: ■ sample 1, □ sample 2, ● sample 3, ○ sample 4, ▼ sample 5, and ▽ sample 6.

However, like the measurements themselves, the measurements of the conditions used were made with different instruments and varying degrees of precision. For this reason, a controlled study of the influence of different measurement conditions is now underway at NIST.

4. Summary   Several studies are underway to improve the accuracy of compound semiconductor composition determinations. Initial focus is on the AlGaAs and InGaAsP material systems. By combining a variety of analysis techniques (RHEED, EMPA, ICP–OES and PL), high accuracy AlGaAs composition standard reference materials are being produced with mole fractions specified to better than ±0.003. The influence of different parameters on measurement methods is being assessed. PL measurements of AlGaAs film composition were found to be sensitive to measurement temperature, excitation intensity, doping concentration and calibration of the photon energy scale and spectrometer response. An interlaboratory comparison of InGaAsP *ex-situ* characterization demonstrated that, for the 1 μm thick films used, material nonuniformity precluded comparison of X-ray analysis from different instruments. However, the PL variation across each sample was smaller than the variation between measurements and allowed differences between measurement systems to be identified.

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